Isotropic superconducting state and high critical currents in $Fe_{1+y}Te_{1-x}S_x$ single crystals.

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We report single crystal growth and a study of superconducting properties in $Fe_{1+y}Te_{1-x}S_x$. We demonstrate the smallest upper critical field anisotropy, $\gamma = H_{c2}^{\|c}/H_{c2}^{\perp c}$, among all iron based superconductors, the value of γ reaches 1.05 at $T = 0.65T_C$ for $Fe_{1.09}Te_{0.89}S_{0.11}$, while still maintaining large values of upper critical field.

The discovery of superconductivity in quaternary iron based layered superconductor $LaFeAsO_{1-x}F_x$ with T_C = 26 K stimulated an intense search for superconductors with higher T_C in this materials class.[1] Shortly after, the critical temperatures were raised up to 55 K in materials of the ZrCuSiAs structure type (Ref. 2), and superconductivity had been discovered in $Ba_{1-x}K_xFe_2As$ and LiFeAs.[3,4]

Superconductivity in the PbO - type FeSe opened another materials space in the search for iron based superconductors.[5] This was followed by the discovery of superconductivity in $FeTe_{1-x}Se_x$ and $FeTe_{1-x}S_x$.[6,7] Iron chalcogenide superconductors with simple binary crystal structure share the most prominent characteristics of iron arsenide compounds: a square planar lattice of Fe with tetrahedral coordination similar to LaFeAsO or LiFeAs, and Fermi surface topology.[8] Superconducting T_C's up to 37 K were discovered with the application of hydrostatic pressure.[9] It was noted, however, that it would be desirable to have isotropic superconductors with high T_c and ability to carry high critical currents for power applications.[10] In this work we report the synthesis of $Fe_{1+y}Te_{1-x}S_x$ ($x = 0-0.14$) superconducting single crystals. We demonstrate small values of $\gamma = H_{c2}^{\|c}/H_{c2}^{\perp c}$ while still maintaining large values of the upper critical field and critical currents.

Single crystals of $Fe_{1+y}Te_{1-x}S_x$ were grown from Te-S self flux using a high temperature flux method.[11,12] Elemental Fe, Te and S were sealed in quartz tubes under partial argon atmosphere. The sealed ampoule was heated to a soaking temperature of 430-450 ^oC for 24h, followed by a rapid heating to the growth temperature at 850-900^oC, and then slowly cooled to 800-840 ^oC. The excess flux was removed from crystals by decanting. Plate-like crystals up to $11 \times 10 \times 2mm^3$ can be grown. Elemental analysis and microstructure was performed using energy dispersive x-ray spectroscopy (EDS) in an JEOL JSM-6500 scanning electron microscope. The average stoichiometry was determined by examination of multiple points on the crystals. Powder X-ray diffraction (XRD) was measured using a Rigaku Miniflex with Cu K_α radiation (λ = 1.5418 Å). The unit cell parameters were obtained by fitting the XRD spectra with the Rietica software.[13] Flux - free rectangular shaped crystals with the largest surface orthogonal to c axis of tetragonal structure were selected for four-probe resistivity measurements. Thin Pt wires were attached to electrical contacts made with Epotek H20E silver epoxy. Sample dimensions were measured with an optical microscope Nikon SMZ-800 with 10 μm resolution. Magnetization and resistivity measurements were carried out in a Quantum Design MPMS-5 and a PPMS-9 for temperatures from 1.8 K to 350 K.

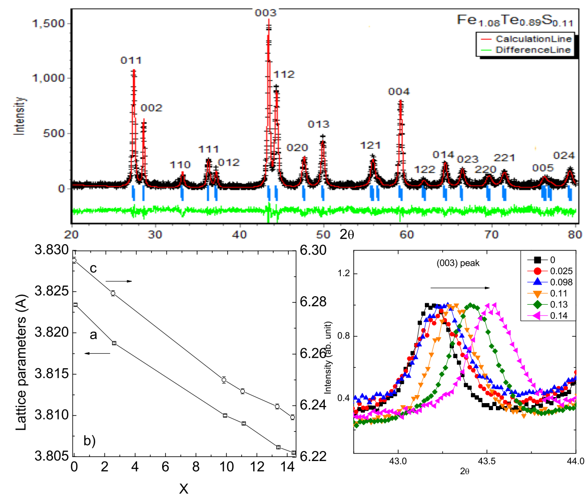

FIG. 1: Powder X-ray diffraction spectra for $x = 0$ and 0.133 samples. The lattice parameters vs. S concentration.

The powder X-ray diffraction patterns for all samples investigated can be indexed in the $P4/nmm$ space group of PbO structure type and small fraction of Te from the flux. Fig. 1(a) shows refinement of $Fe_{1.09}Te_{0.89}S_{0.11}$. The calculated diffraction pattern shows excellent agreement with the experiment and high phase purity. The lattice parameters are shown in Fig. 1(b). Both the a and c axis decrease uniformly with x, conforming with Vegard's law. Fig. 1(c) shows uniform evolution of [003] peak with sulfur content, consistent with the decreasing c axis parameter. Thus S doping is equivalent to a positive

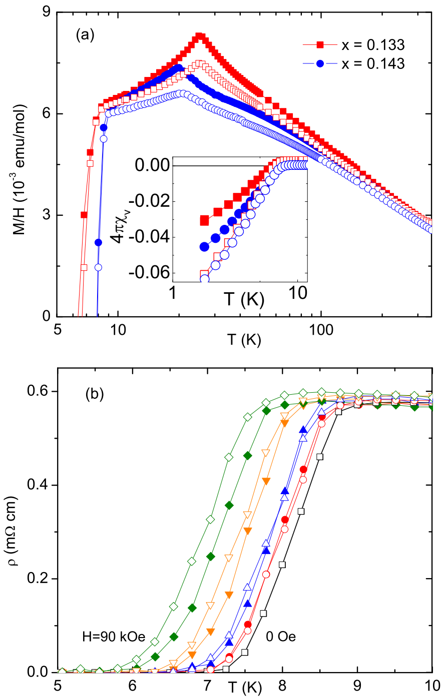

FIG. 2: a) Temperature dependence of magnetic susceptibility of two superconducting samples ($x = 0.133$ and 0.143) for $H \perp c$ (solid symbols) and $H \parallel c$ (open symbols). Inset shows the volume fraction of the as a function of temperature (1.8-12 K). b) In-plane resistivity for $x = 0.133$ of two field orientations.

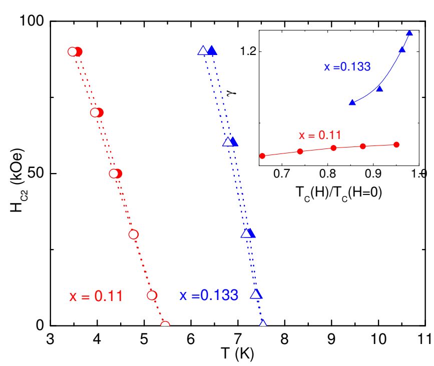

FIG. 3: The upper critical fields for $x = 0.011$ and 0.133. Dotted lines are guides to the eye. Inset shows the anisotropy in the upper critical field $\gamma = H_{c2}^{\parallel c}/H_{c2}^{\perp c}$.

chemical pressure and reduces the unit cell volume by up to 2%. The compositions from EDS are presented in Table I. The excess Fe decreases with increasing S content.

Fig. 2 (a) shows the temperature dependence of the magnetic susceptibility for a magnetic field applied in the ab plane and along c axis. Magnetic transition is suppressed to 25 K, as was observed in $FeTe_{1-x}S_x$ polycrystals.[7] Superconductivity is observed

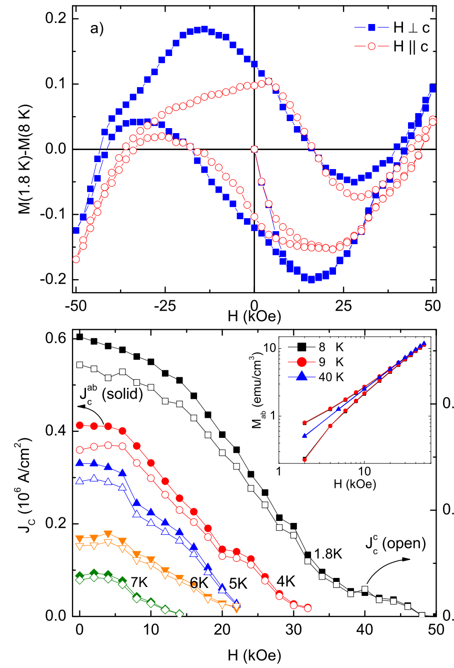

FIG. 4: a) Magnetization hysteresis loops of $x = 0.133$ for $1.8K$ after ferromagnetic background subtraction for $H//c$ (open symbols) and $H \perp c$ (solid symbols). b) In-plane (to left axis) and interplane (to right axis) critical currents for $x = 0.133$. Inset shows the magnetization at 8, 9 and 40 K. Only the positive field magnetization is shown on log-log scale and the virgin curves of the loops at 8 and 9 K are omitted for clarity.

for $x \geq 0.11$. The volume fraction $4\pi\chi_v$ reaches $-0.06 \sim -0.09$ at 0 K by linear extrapolation. Considering that the estimated superconducting volume fraction is only up to 10%, we speculate that the superconducting phase may exist in fractional domains associated with S atoms. With more S-doping, these domains are gradually connected to form a full superconducting path for electrical transport, as it was observed in $CaFe_{1-x}Co_xAsF$.[14,15]

The temperature dependence of resistivity with a magnetic field applied perpendicular and parallel to c axis is shown in Fig. 2 for $x = 0.133$. The residual resistivity of the normal state $\rho_0 = 0.58m\Omega cm$ of our crystals is smaller than that is observed in polycrystalline $FeTe_{1-x}S_x$.[7] It is comparable with residual resistivity observed in $NdFeAsO_{0.7}F_{0.3}$ ($\sim 0.2m\Omega cm$)[16] or $(Ba_{0.55}K_{0.45})Fe_2As_2$ ($\sim 0.4m\Omega cm$)[17] single crystals. Transition width of our crystals ($\Delta T_c = T_{onset} - T_{zero\rho} = 1.8K$) is smaller than that in Ref. 7 ($\Delta T_c = 2K$). The small shift of the transition temperature with magnetic field indicates a large zero-temperature upper critical field. The upper critical field H_{c2} is estimated as the field corresponding to the 90% of resistivity drop (Fig.3). An estimate for $H_{c2}(T = 0)$ is given by weak-coupling formula for conventional superconductors

x	y	$H_{c2}^{'\perp c}(T_c)$	$H_{c2}^{\perp c}(0)(T)$	$H_{c2}^{'\parallel c}(T_c)$	$H_{c2}^{\parallel c}(0)(T)$	$\xi^{\perp c}(0)(nm)$	$\xi^{\parallel c}(0)(nm)$
0	0.15(3)						
0.110(6)	0.09(3)	−4.9	19	−4.6	18	4.3	4.3
0.133(6)	0.08(3)	−10.7	56	−8.4	44	2.4	2.7

TABLE I: EDX analysis results , upper critical field at zero temperature and corresponding coherence length.

in the Werthamer-Helfand-Hohenberg model (Table I): $H_{c2o}(0) \sim -0.7H_{c2}^{'}(T_c)T_c$.[18] The superconducting coherence length $\xi(0K)$ $[\xi^2 = \Phi_0/2\pi H_{c2}]$ is around 3 nm. The anisotropy $\gamma = H_{c2}^{\parallel c}/H_{c2}^{\perp c}$ decreases with a temperature decrease approaching a value close to unity. By $T_c/T_c(0) \approx 0.65$ (Fig. 3(inset)), $\gamma = 1.05$, for $x = 0.11$. These values indicate that $FeTe_{1-x}S_x$ is a high field isotropic superconductor, with γ smaller than that in Ref. 19 ($\gamma > 1.5$ at $0.5T_C(H = 0)$) or in Ref. 20 ($\gamma \sim 1.3$ at $0.5T_C(H = 0)$).

To determine the anisotropy of the critical current, we analyze the magnetic measurements using an extended Bean model.[21,22] Considering a rectangular prism-shaped crystal of dimension $c < a < b$, when a magnetic field is applied along the crystalline c axis, the in-plane critical current density j_c^{ab} is given by

$$j_c^{ab} = \frac{20}{a}\frac{\Delta M_c}{(1 - a/3b)}$$

in which ΔM_c is the width of the magnetic hysteresis loop for increasing and decreasing field. When the magnetic field is applied along the b axis and parallel to the ab plane, both of the in-plane j_c^{ab} and the cross-plane j_c^c are involved in the Bean model. For a crystal in our measurements with $a = 1.245mm, b = 1.285mm$ and $c = 0.732mm$,

$$j_c^c = \frac{c}{3a}\frac{j_c^{ab}}{(1 - 20\Delta M_b/cj_c^{ab})}$$

Because of the large volume fraction of the normal and magnetic state, a magnetic background is superposed on the hysteresis loop. Moreover, as shown in Fig. 4 (b) inset, the hysteretic magnetisation loop for the sample $x = 0.133$ sustains above the superconducting transition temperature at 7.5 K and vanishes above the antiferromagnetic transition at 25 K. It implies a magnetic structure of $FeTe_{1-x}S_x$ where a ferromagnetic component coexists with an antiferromagnetic moment. Density functional calculation on FeTe by Alaska Subedi et al does indicate that besides the SDW, FeTe is close to a ferromagnetic instability, similar to LaFeAsO.[23] In order to estimate the ΔM only due to flux pinning, we take the hysteresis loop immediately above superconducting transition at 8 K as the ferromagnetic background and subtract it from other loops below 7.5 K. The identical hysteresis loops at 8 and 9 K in the normal state justifies our rationale to use them as a temperature independent background. Fig. 4(a) shows hysteresis loops for $H//c$ and $H \perp c$ at 1.8 K after background removal. The magnetically deduced in-plane and interplane critical current density are displayed in Fig. 4(b). The ratio of j_c^{ab}/j_c^c is roughly about 4. The critical current densities for both directions are $10^5 - 10^6 A/cm^2$, comparable to MgB_2, $Ba(Fe_{1-x}Co_x)_2As_2$ in the same temperature range[24].

In summary, we show that $FeTe_{1-x}S_x$ are isotropic high field superconductors with one of the smallest values of $\gamma = H_{c2}^{\parallel c}/H_{c2}^{\perp c}$ observed so far in iron based superconducting materials . Moreover, anisotropy in the superconducting state decreases with increased sulfur content. By utilizing high pressure synthesis techniques even higher T_C's, upper critical fields and smaller γ may be simultaneously obtained. Since $FeTe_{1-x}S_x$ superconductors consist of relatively inexpensive and nontoxic elements they may represent future materials of choice for high field power applications.

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